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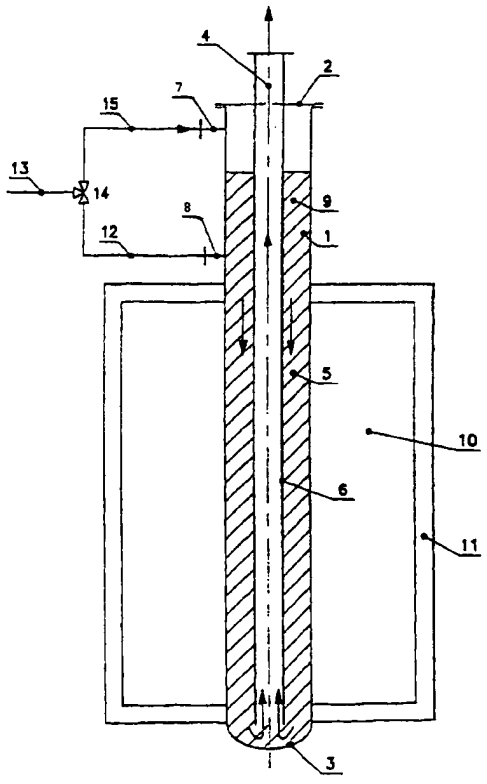
(54) Title: CATALYST TUBES FOR ENDOTHERMIC REACTION ESPECIALLY FOR THE PRODUCTION OF HYDROGEN AND SYNGAS



(57) Abstract: A regenerating catalytic tube including an outside tube (1), whose ends are sealed by a head flange (2) and a bottom (3), and a second tube (6) which is located coaxially within outside tube (1) so that one end thereof is placed near bottom (3) and the other end terminates outside closure flange or plate (2), the hollow space between coaxial tubes (1 and 6) being filled with a catalyst material (5) which is crossed by the material to be processed during the catalytic reaction and comprising a portion capable of being lapped by a heating medium, and a non-heated portion which is capable of a thermal exchange exclusively between the product (flowing in the output line (4)) of the endothermic reaction and the material to be processed (entering through input line (7)), does not contact the heating medium inside the radiative chamber itself.

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

CATALYST TUBES FOR ENDOTHERMIC REACTION ESPECIALLY FOR THE PRODUCTION OF HYDROGEN AND SYNGAS

The present invention relates to an improved regenerating catalytic tube for endothermic reactions, particularly for the production of hydrogen and syngas.

European Patent 0 817 673 issued to the same Applicant of this invention discloses a regenerating catalytic tube including an outside tube which has one closed end and is capable of being heated from the outside, for example by combustion gas, to bring and keep the material to be treated to the reaction temperature. A second tube is coaxially located within the outside tube with its lower end terminating at a distance from the bottom of the outside tube.

The hollow space between such coaxial tubes is filled with a catalyst so that the fluid to be processed entering the outside tube through an appropriate entrance near its upper end passes through the whole catalyst up to the bottom of the outside tube and is subjected to the catalytic reactions, whereupon it passes through the internal coaxial tube without catalyst and further through the conduits of the treatment plant.

In particular, the upper end of such outside tube is secured and closed by a head flange having a central through hole for receiving the inside coaxial tube

carrying the treated material downstream of the catalytic tube.

The catalytic reaction is endothermic and ends as soon as the fluid to be treated reaches the bottom of the outside tube and enters the inside coaxial tube for rising to the output.

Thus, a significant amount of heat contained in the material already subjected to the catalytic process is given to the reaction area absorbing heat from both the outside by the combustion gases and the inside by the energy regenerated by the treated product rising to the output of the catalytic tube.

In order to maximize the heat exchange between the product and the material to be processed, the above-mentioned European Patent claims a particular geometry of the rise tube of the reaction product.

Although the resulting energy regeneration improves the efficiency of the thermal exchange and the utilization of the heat delivered by the plant to the catalytic tube, the material to be treated should be fed to the catalytic tube at very high temperatures and the product provided by the catalytic reaction should be cooled before being fed to the next treatment stations. In addition to the pre-reaction heating and post-reaction cooling costs this also causes further costs due to the need of using materials having high mechanical and chemical resistance at high temperatures.

The present invention seeks to provide some

construction and operational improvements to the known catalytic tube described above by providing a tube capable of treating input materials and output products at temperatures which are considerably lower than those commonly used in the known installations.
This advantageously causes a reduction in the operating and manufacturing costs of the plant since it is possible to avoid or strongly reduce preheating and post-cooling and then the relative apparatus. In addition, the design and the construction of the plant piping are simplified as the conduits operate at considerably lower temperatures than the current installations.

A better understanding will result from the following detailed description with reference to the accompanying drawings that show some preferred embodiments only by way of a not limiting example.
In the drawings:

Fig. 1 shows a longitudinal section of the known catalytic tube according to the European Patent 0 817 673;

Fig. 2 shows a longitudinal section of the improved regenerating catalytic tube according to the invention;

Fig. 2A shows cross sections of the tube according to some preferred embodiments of the invention;

Fig. 3 shows a regenerating catalytic tube installed in the radiative chamber of an oven;

Fig, 4 shows an alternative embodiment of the invention in which the material to be processed is fed by two pipes at different heights;

Fig. 5 shows schematically a plant of the conventional type; and

Fig. 6 shows the processing diagram of a plant embodying the present invention.

With reference to Fig. 1, a regenerating catalytic tube according to the European Patent 0 817 673 consists of a long outside tube 1 whose length varies only by way of example from 3 to 14 m and can be heated by combustion gases from the outside.
The two ends of the tube are sealed by head flange 2 and bottom 3. A vertical rise tube 6 having its axis coincident with that of catalytic tube 1 is located within tube 1 and ends at the lower portion of the latter where there is a passage near bottom 3.
At the upper end vertical tube 6 passes through head flange 2 and forms output tube 4. Located under the head flange is supplying pipe 7 for feeding the material to be processed. The product formed as a result of the catalytic reactions is removed through rise tube 6 and output tube 4.

The hollow space between the inside surface of catalytic tube 1 and the outside surface of rise tube 6 is filled with a catalyst 5 through head flange 2. The material to be processed is heated until the reaction temperature is reached, and the endothermic reaction is carried out by the heat provided by the combustion gases. The endothermic reaction ends as soon as the treated material leaves the catalyst bed 5 above bottom 3. The flux direction of the material is here reversed and the product is carried upwards through rise tube 6 and is removed through output tube 4.

The product moving upwards in the rise tube 6 transfers heat to the material to be processed through the wall of rise tube 6. In this way a significant amount of the heat of the product can be recovered and used to perform the endothermic reaction. Rise tube 6 is provided with such a geometry as to maximize the heat exchange between the product and the material to be processed, as disclosed in the above-mentioned patent.

The present invention makes use of a regenerating catalytic tube of the type mentioned above, however, it provides the solution of locating the inlet of the material to be processed and the outlet of the treated product at the outside end of the radiative chamber where the catalytic tubes to be heated are immersed.

The basic inventive step of the invention is to provide a heat exchange exclusively between the treated output product and the process material fed

into said outside end, the contact with the combustion gases inside the radiative chamber being avoided.

With particular reference to Fig. 2, the regenerating catalytic tube according to the present invention includes an outside tube 1 closed at one end by a bottom 3 able to be heated from the outside preferably by combustion gas while the other end is closed by a removable flange 2.

A second tube 6 smaller that the first tube is located coaxially inside the outside tube 1 and has one end near bottom 3 and the other end outside the closing flange or plate 2. A catalyst material 5 is put in the hollow space between the two coaxial tubes 1 and 6 so as to be crossed by the material to be processed during the catalytic reaction.

Fig. 2A shows only by way of a not limiting example several types of cross sections of catalytic tubes which differ from one another essentially by the presence of an inside tube having different sections to improve the thermal exchange between the reaction area where catalyst 5 is placed and the output tube 6 of the final product, in order to increase the heat amount which is given by the reaction product to the reaction area.

As can still be seen in Fig. 2, the material to be processed is put into the hollow space containing catalyst 5 through an input pipe 7 located under flange 3.

The arrows schematically show the path of the material to be treated during the catalytic reaction. After the

entrance into the hollow space, the material to be reacted flows down (in the figure) through the whole catalyst until bottom 3 of outside tube 1 is reached, from which it rises through inside tube 6 to output 4 of flange 2. During such rise path to the output the further already described thermal exchange takes place for giving heat to the reaction area.

According to a further feature of the invention, inert material 9 such as alumina balls or the same catalyst is put into the hollow space portion between inside and outside tubes 6, 1 located between input tube 7 and refractory wall 11 of the radiative chamber. Since a heat exchange occurs in that area outside the radiative chamber only between the outgoing reaction product and the incoming material to be processed, such inert material 9 or catalyst acts only as heat exchange promoter causing turbulence in the flow of the material to be processed.

Thus, the material to be processed is advantageously preheated before entering the reaction area, while the reaction product is cooled after the output from the reaction area itself. This allows the process material to be fed at temperatures which are considerably lower than those commonly used and at the same time to provide the product at temperatures which are considerably lower than those typically used.

From the foregoing it is self-evident that the portion of catalytic tube 1 which is not exposed to fire or is located outside radiative chamber 10 can advantageously be made of a material which is less

expensive than that necessary for the portion of catalytic tube 1 immersed in the above-mentioned radiative chamber.

Furthermore, the presence of a tube length outside radiative chamber 10, in which the thermal exchange for preheating the material to be processed takes place and the reaction product is cooled, allows heater 33 upstream of catalytic tube(s) 1 and cooling apparatus 36 downstream of the same to be advantageously removed from the plant.

According to an alternative embodiment of the invention schematically shown in Fig. 4, an input 8 for the material to be processed is additionally provided in catalytic tube 1. Such input 8 placed near refractory wall 11 of radiative chamber or oven 10 has the function of allowing the output temperature of the product to be controlled.

By the way it should be noted that the material from pipe 13 to be processed can be fed to one or both input pipes 7 and 8 through a three-way valve 14 and pipes 12 and 15. In particular, if the whole material to be processed is fed to catalytic tube 1 exclusively through input pipe 7, the heat exchange between the product and the material to be processed will be maximum and then the product will come out of output tube 4 at an as low as possible temperature considering the characteristics of the surface of thermal exchange and the heat transfer rate.

However, if the material to be processed is fed into catalytic tube 1 only through additional input pipe 8,

no thermal exchange between the product and the material to be processed will take place in the portion of the catalytic tube above input pipe 8, and the product will flow out of the output tube 4 at the temperature set by the thermal exchange occurred between product and material to be processed in the portion of catalytic tube 1 under input pipe 8.

Therefore, the output temperature of the product at the output tube 4 can be continuously controlled between the minimum and maximum value by a suitable distribution of the material to be processed by three-way valve 14 to input pipe 7 and input pipe 8 and pipes 12 and 15.

As already mentioned, the present invention allows the steam reforming ovens and particularly the plants for the production of hydrogen and syngas to be advantageously and significantly improved.

Fig. 5 schematically shows the process diagram of a conventional plant of the type currently used for the production of hydrogen and syngas from a hydrocarbon charge.

Actually, a hydrocarbon charge fed to the plant is desulphurized 31, mixed with steam 32 and preheated in the convective section 33 of the reforming oven and then conveyed to the catalytic tubes of steam reforming oven 34. The latter operates under somewhat severe temperature and pressure conditions (up to 950°C and 60 bar). The effluent from the catalytic tubes of the steam reforming oven should be fed to boiler 36 through manifold 35 operating at high

temperatures. Such boiler 36 cools the gas at a suitable temperature for the next catalytic conversion of carbon monoxide 37.

Fig. 6 shows the process diagram of a plant embodying the present invention. Just looking at this figure where the suppressed apparatus are shown in broken lines and comparing the same with Fig. 5, the following advantages over the known plants are pointed out:

- the expensive manifolds 35 operating at high temperatures for dispensing the material to be processed to regenerating catalytic tubes 1 and for collecting the output product from such catalytic tubes are suppressed;
- in case of plant for the production of hydrogen or syngas made according to the invention, the product is extracted from catalytic tubes 1 at temperatures lower than 350°C, thus strongly reducing the danger of dust corrosion during the cooling of the product which takes place in some tenth of second;
- preheater 33 of the material to be processed is removed;
- product cooler 36 is removed or strongly simplified;
- in case of plant for the production of hydrogen, the product obtained according to the invention can be fed directly to the converter of carbon monoxide 37.

It should be appreciated that the invention further allows the consumption of fuel to be reduced under the same yield of hydrogen or syngas because of the regeneration of the heat of the reaction product for

preheating the material to be processed, thus causing a reduction of the amount of polluting agents present in the flue gas discharged to the atmosphere.

At last, the invention allows advantageously the yield of the known plants to be increased without construction modifications of the steam reforming oven but with the only modification of the already existing catalytic tubes by using the special arrangement of rise tubes 6 described above.

The invention has been described and illustrated according to preferred embodiments thereof, however, it should be understood that those skilled in the art can make equivalent modifications and/or replacements without departing from the scope of the present industrial invention.

For example, the disclosed tube could be used for improving the known plants of the conventional type without using the portion of heat exchange between product and material to be processed outside the radiative chamber, thus obtaining an increase of the thermal efficiency by the inside coaxial tube 6 that regenerates partially the heat of the reaction product.

Claims

1. An improved regenerating catalytic tube for endothermic reactions, particularly for the production of hydrogen and syngas, comprising an outside tube (1) closed at one end by a bottom (3) while the other end is closed by a removable flange (2), and a second tube (6) located coaxially inside the outside tube (1) and having the inside end near bottom (3) and the outside end terminating outside the closing flange or plate (2), a catalyst material (5) being filled in the hollow space between the two coaxial tubes (1 and 6) so as to be crossed by the material to be processed during the catalytic reaction, characterized by a portion capable of being lapped by a heating medium by radiance and/or conduction and/or convection, and by a non-heated portion which is capable of a thermal exchange exclusively between the product of the endothermic reaction and the material to be processed.

2. The improved catalytic tube according to claim 1, characterized in that said non-heated portion, where at least one input pipe (7) for the material to be processed and one output pipe (4) for the treated product are provided, is located outside a radiative chamber (10) where the other outside portion is immersed to be heated at the reaction temperature, any contact with the combustion gases inside the radiative chamber being avoided for said non-heated portion.

3. The improved catalytic tube according to the preceding claims, characterized in that said heating medium is combustion gas.

4. The improved catalytic tube according to claims 1 and 2, characterized in that said heating medium is high-temperature gas.

5. The improved catalytic tube according to claims 1 and 2, characterized in that the inside coaxial tube (6) has a circular or elongated or undulated cross section able to improve the thermal exchange between the reaction area, where catalyst (5) is located, and output tube (6) of the final product so as to increase the amount of heat which is given from the reaction product to the material to be processed.

6. The improved catalytic tube according to claims 1 and 2, characterized in that an input pipe (7) of the material to be processed in the hollow space with catalyst (5) is placed under flange (2) so that the reaction material passes through the hollow space and catalyst (5) maintained at the reaction temperature until bottom (3) of outside tube (6) is reached, from which it rises along inside tube (6) to output tube (4) outside flange (2), a further thermal exchange that gives heat to the reaction area taking place during the latter path.

7. The improved catalytic tube according to the

preceding claim, characterized in that inert material (9) acting as heat exchange promoter causing turbulence in the flow of the material to be processed is put into the portion of the hollow space between input pipe (7) and a refractory wall (11) of radiative chamber (10), a heat exchange occurring in that area of the catalytic tube outside radiative chamber (10) only between the outgoing reaction product and the incoming material to be processed.

8. The improved catalytic tube according to the preceding claim, characterized in that said inert material (9) consists of alumina balls or the catalyst (5) itself.

9. The improved catalytic tube according to claim 7 or 8, characterized in that the material to be processed is preheated before the entrance into the reaction area, while the reaction product is cooled after the output from the reaction area, the material to be processed being fed at temperatures which are much lower than those commonly used and at the same time the product being extracted at temperatures which are much lower than those typically used.

10. The improved catalytic tube according to claims 1, 2, 6, 7, 8 and 9, characterized in that an input (8) for the material to be processed is additionally provided in catalytic tube (1) near refractory wall (11) of radiative chamber or oven 10 with the function

of allowing the output temperature of the product to be controlled by the regulation of the thermal exchange occurring outside radiative chamber (10).

11. The improved catalytic tube according to the preceding claim, characterized in that the material to be processed from pipe (13) is conveyed to one or both input pipes (7 and 8) through a three-way valve (14) and suitable connecting pipes (12 and 15) so that the output temperature of the product from output tube (4) is controlled continuously by distributing the material to be processed to input pipes (7 and 8).

12. The improved catalytic tube according to the preceding claims,, characterized in that the renewal or the expansion of the existing plants of conventional type is allowed with or without using the portion of thermal exchange between product and material to be processed outside the radiative chamber without any construction modification to the radiative chamber of the existing plants.

13. A plant for the production of syngas or hydrogen from a hydrocarbon charge, characterized in that there is provided the use of catalytic tubes according to the preceding claims.

14. The plant of the preceding claim, characterized in that the hydrocarbon charge desulphurized and mixed with steam is fed directly to the catalytic tube(s) of

a steam reforming oven, the effluent of the latter being fed directly to an apparatus for the catalytic conversion of carbon monoxide so that:

- the expensive manifolds operating at high temperatures for dispensing the material to be processed to regenerating catalytic tubes and for collecting the output product from such catalytic tubes are suppressed;
- the preheater of the material to be processed is removed;
- the product cooler is removed or strongly simplified;
- the danger of dust corrosion during the cooling of the product which takes place in some tenth of second is strongly reduced.

PRIOR ART

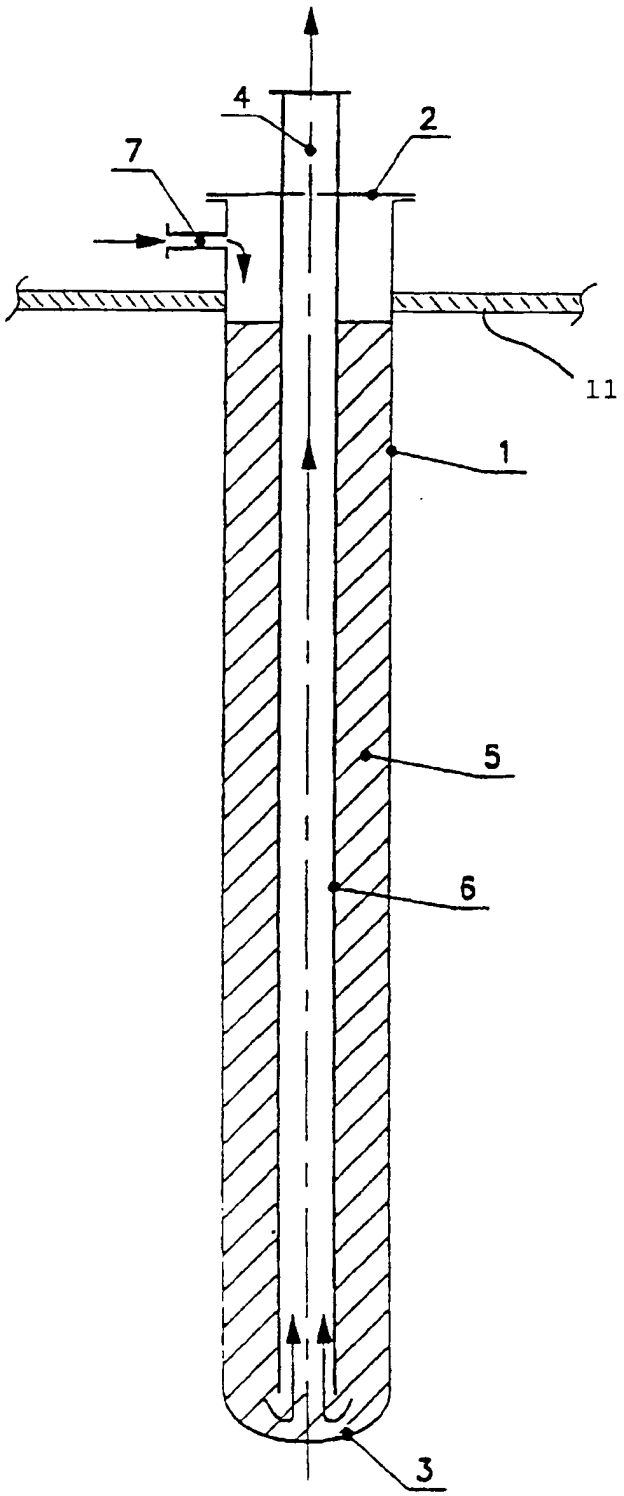

FIG. 1

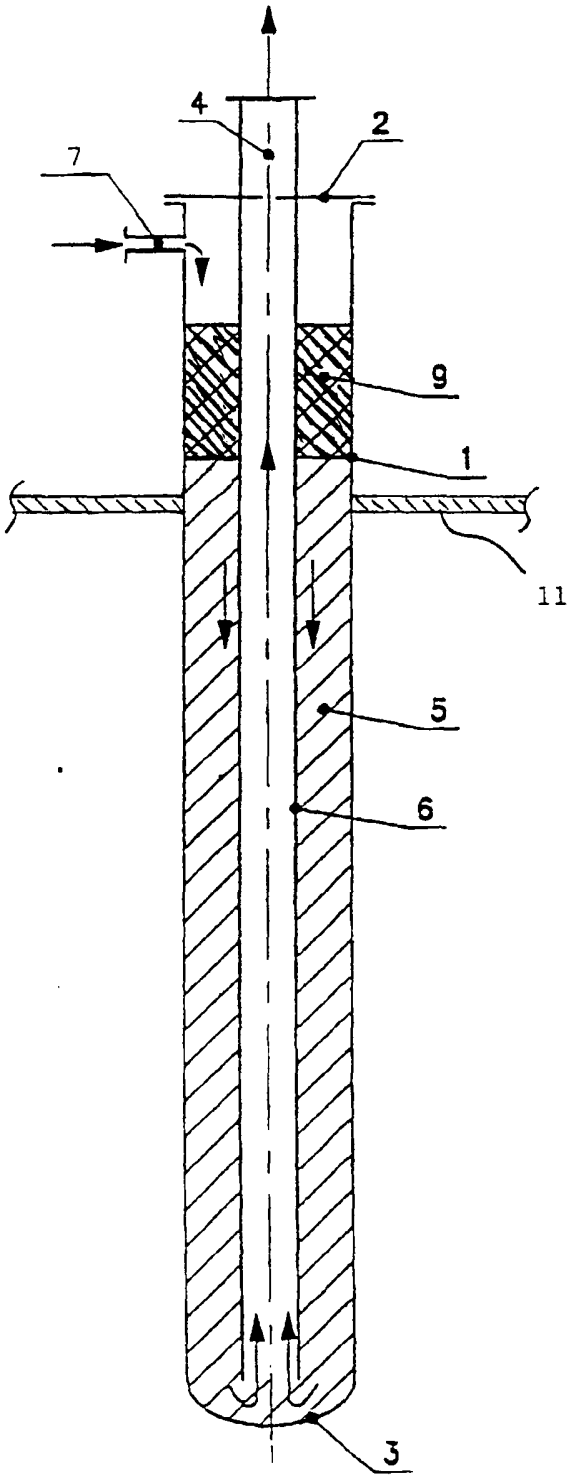

FIG. 2

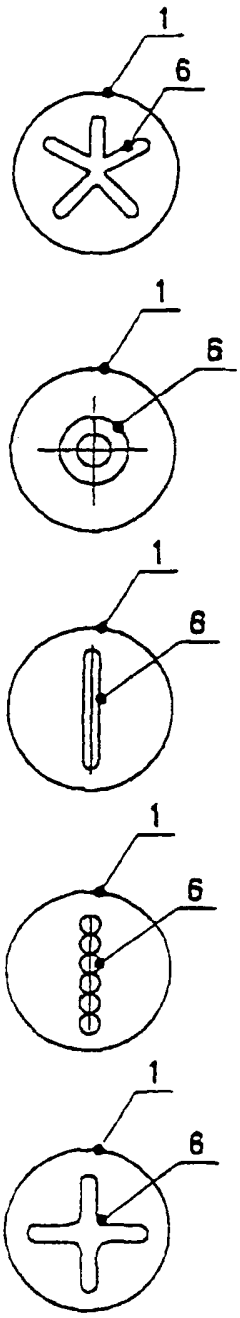

FIG. 2A

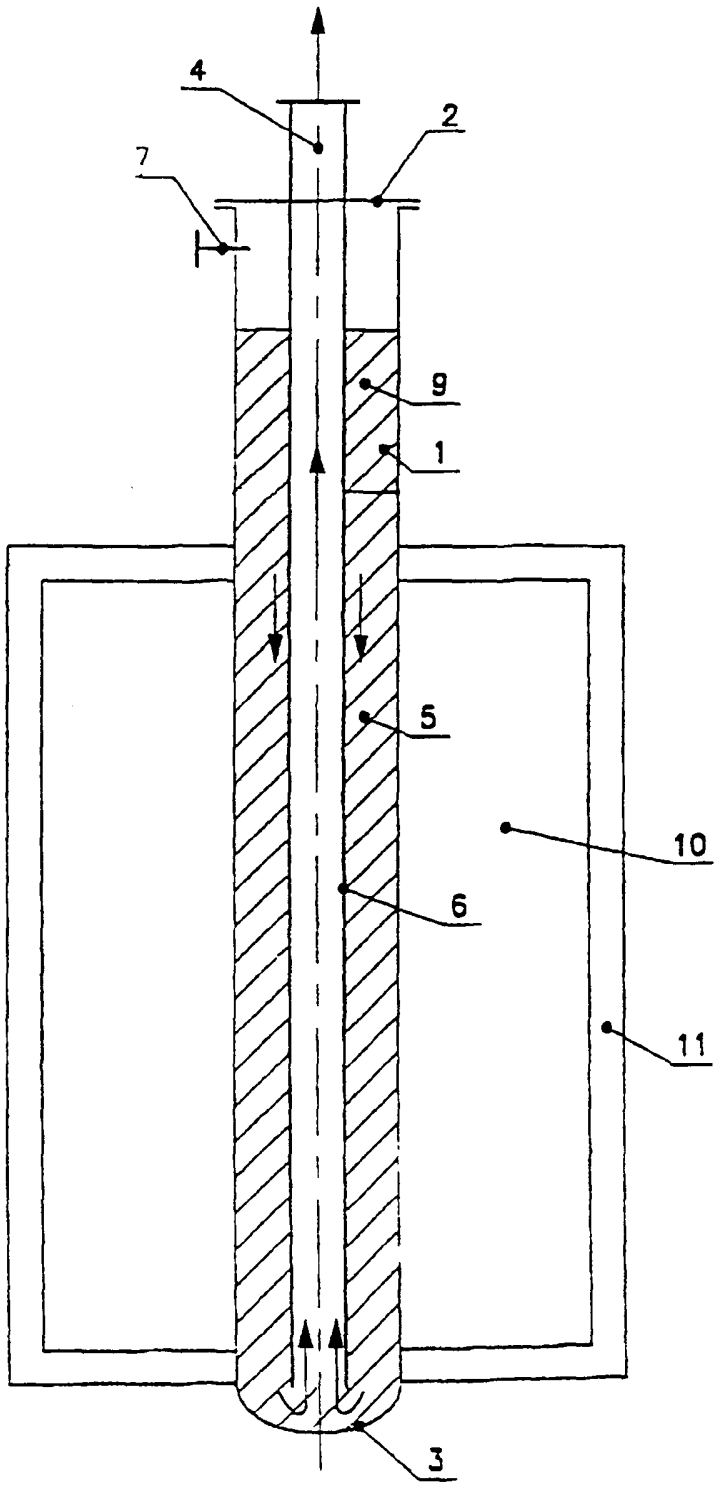

FIG. 3

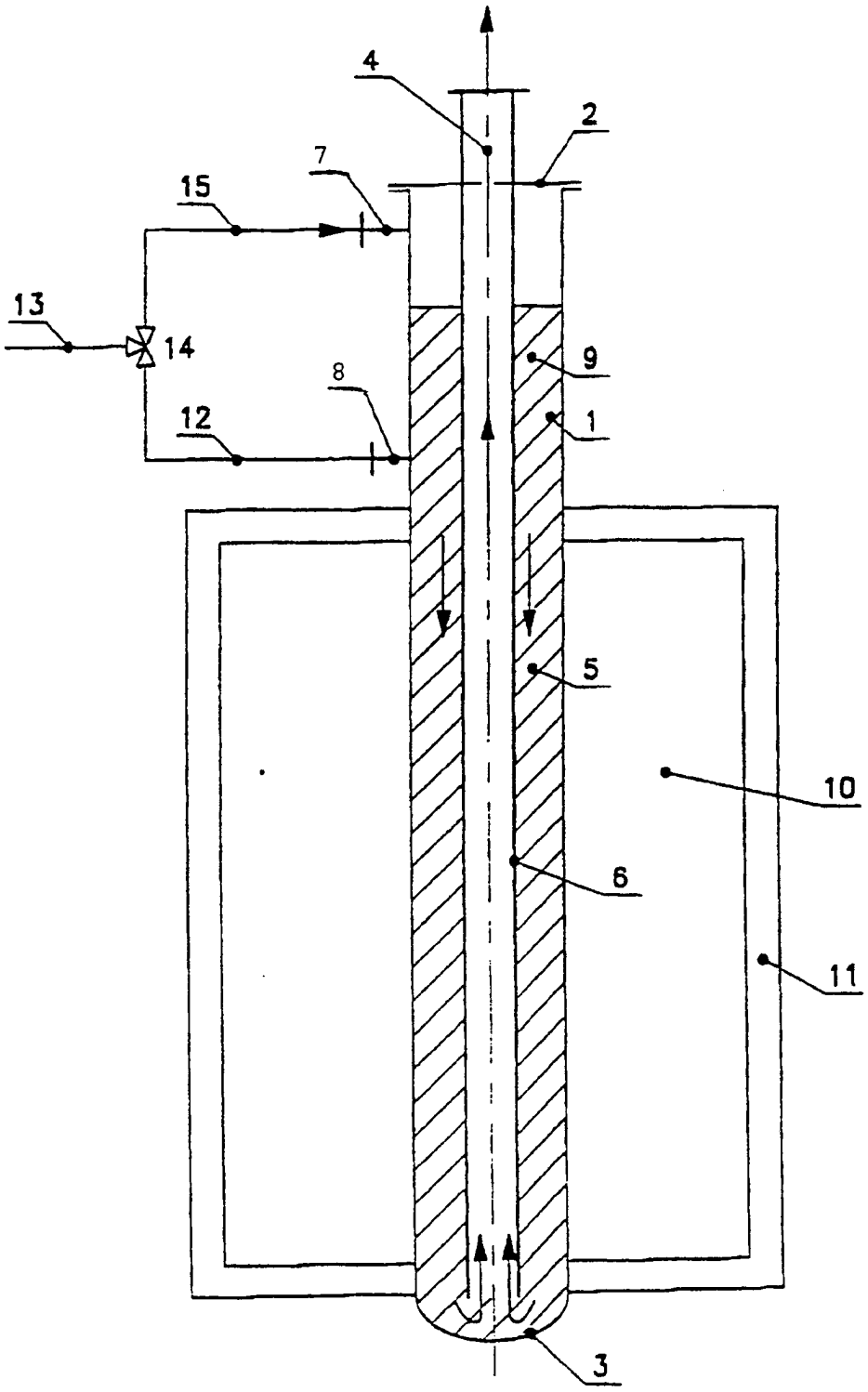

FIG. 4

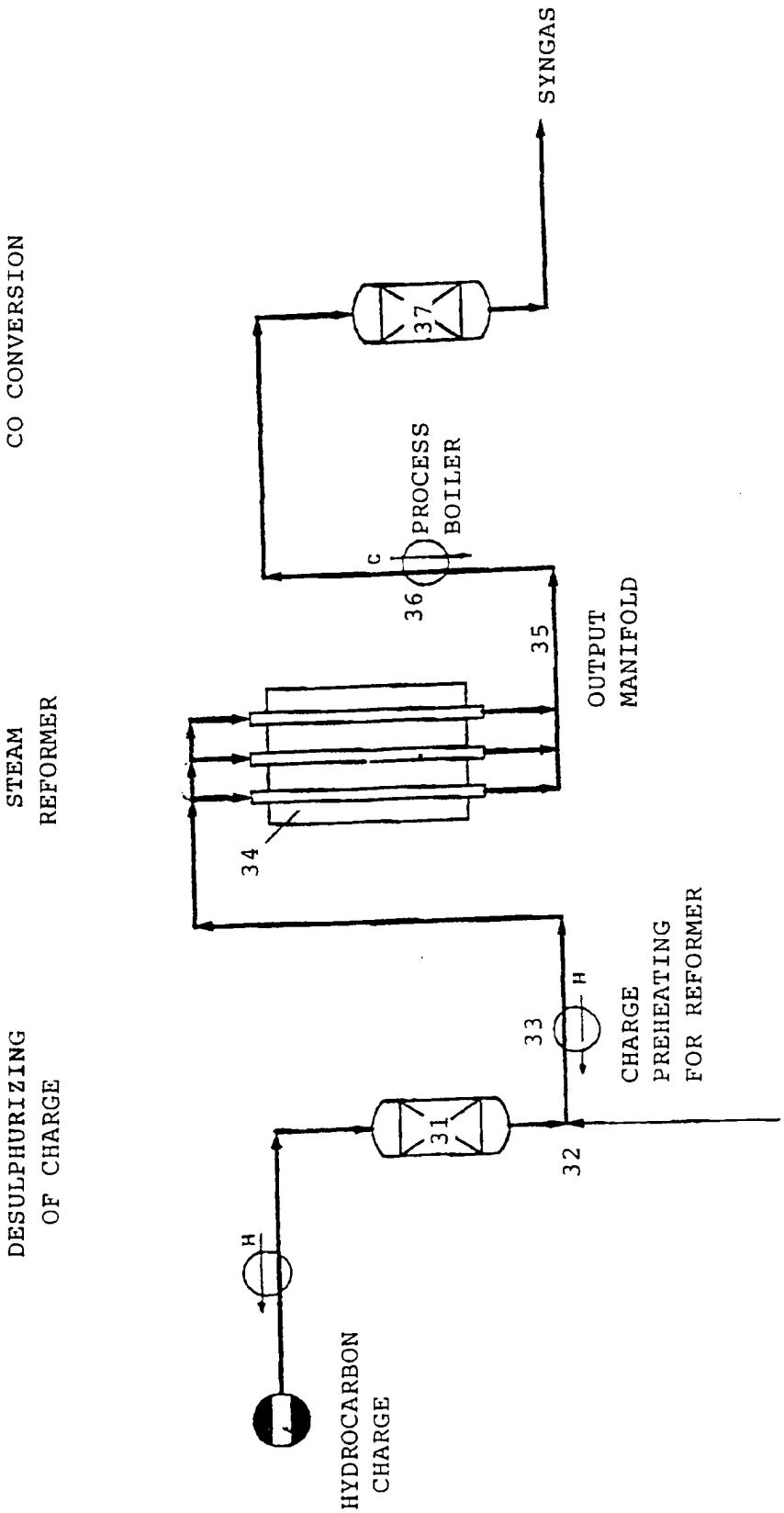
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FIG. 5

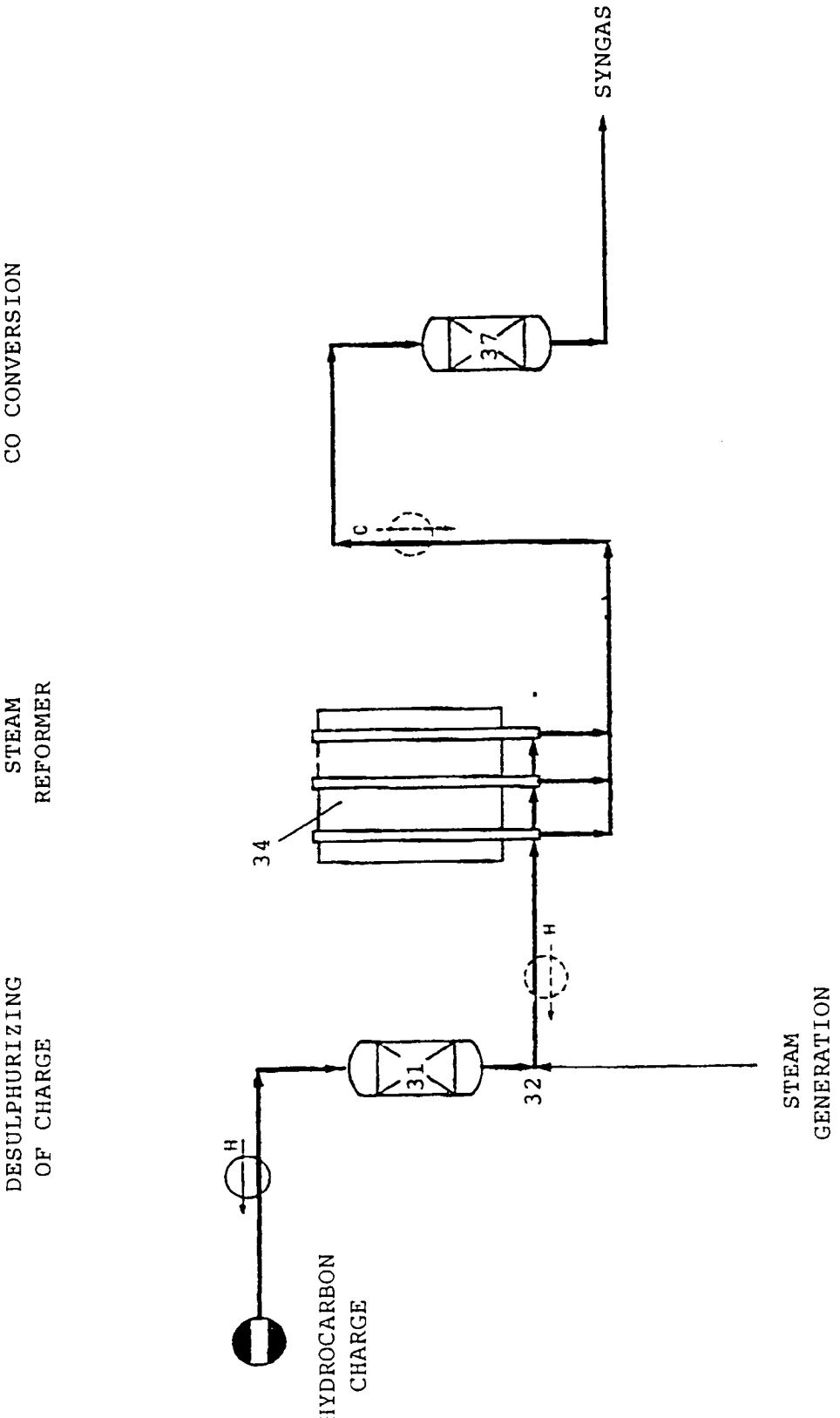
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FIG. 6

INTERNATIONAL SEARCH REPORT

Inte ional Application No
PCT/IT 99/00266

A. CLASSIFICATION F SUBJECT MATTER
IPC 7 B01J8/06 C01B3/38 B01J8/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 B01J C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
12 May 2000	25/05/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Vlassis, M

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INTERNATIONAL SEARCH REPORT

Int: ional Application No
PCT/IT 99/00266

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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Information on patent family members

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